RESULTS OBTAINED WITH THE CORRELATION ENERGY DENSITY FUNCTIONALS OF BECKE AND LEE, YANG AND PARR

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Received 16 December 1988; in final form 17 February 1989

Two recently published density functionals (A.D. Becke, J. Chem. Phys. 88 (1988) 1053 and C. Lee, W. Yang and R.G. Parr, Phys. Rev. B 37 (1988) 785) are used to calculate the correlation energies of first-row atoms, ions and molecules. The correlation contributions to ionization energies, electron affinities and dissociation energies thus obtained are of comparable quality to those of other density functionals.

1. Introduction

Recently two new correlation energy density functionals (DFs) were published: one by Becke [1] (hereafter referred to as B) and one by Lee, Yang and Parr [2] (denoted here as LYP). They both differ from commonly used DFs (such as those of refs. [3–9]) by not using the electron gas as the reference system, but considering instead short-range effects in the two-particle density matrix. While B is derived by assuming a model form of the exchange-correlation hole, LYP was obtained (as the Colle–Salvetti DF [10], from which it originates) from a specific type of correlated wavefunction.

The present paper presents a systematic test of these functionals, by calculating correlation contributions to ionization energies, ΔIE, electron affinities, ΔEA, and dissociation energies, ΔD_e, which were considered previously for various other DFs [11]. Some of the total correlation energies were published in the original papers [1,2].

2. Methods

A Hartree–Fock calculation is first performed to obtain the density. The DFs are then computed using numerical integration. The explicit form of the functionals is as follows (in atomic units):

(a) The functional B [1] is given by

$$E_{\mathrm{c}}^{\alpha\beta+\beta\alpha} = -0.8 \int \rho_\alpha \rho_\beta z_{\alpha\beta}^2 \left(1 - \frac{\ln(1+z_{\alpha\beta})}{z_{\alpha\beta}}\right) \mathrm{d}^3 r\,,$$

$$E_{\mathrm{c}}^{\sigma\sigma} = -0.01 \int \rho_\sigma D_\sigma z_{\sigma\sigma} \left(1 - \frac{2}{z_{\sigma\sigma}} \ln(1+\tfrac{1}{2} z_{\sigma\sigma})\right) \mathrm{d}^3 r\,,$$

$$E_{\mathrm{c}} = E_{\mathrm{c}}^{\alpha\beta+\beta\alpha} + E_{\mathrm{c}}^{\alpha\alpha} + E_{\mathrm{c}}^{\beta\beta}\,, \tag{1}$$

where

$$z_{\alpha\beta} = c_{\alpha\beta}(R_{\mathrm{F}}^{\alpha} + R_{\mathrm{F}}^{\beta})\,, \quad z_{\sigma\sigma} = c_{\sigma\sigma} 2 R_{\mathrm{F}}^{\sigma}\,,$$

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$$R_{\mathrm{F}}^{\sigma}=\frac{1}{\langle s_{\sigma}^{-1}\rangle}\,,\quad \langle s_{\sigma}^{-1}\rangle=3\left(\frac{3}{4\pi}\right)^{1/3}\rho_{\sigma}^{1/3}+2a\frac{(\nabla\rho_{\sigma})^{2}}{\rho_{\sigma}^{7/3}}\left(1+b\frac{(\nabla\rho_{\sigma})^{2}}{\rho_{\sigma}^{8/3}}\right)^{-4/5}\,,$$

$$D_{\sigma}=\tau_{\sigma}-\frac{1}{4}\frac{(\nabla\rho_{\sigma})^{2}}{\rho_{\sigma}}\,,\quad \tau_{\sigma}=\sum_{i_{\sigma}}|\nabla\psi_{i_{\sigma}}|^{2}\,,$$

$$c_{\alpha\beta}=0.63\,,\quad c_{\sigma\sigma}=0.96\,,\quad a=0.00375\,,\quad b=0.007\,.$$

Here σ stands for α or β; ρ_α and ρ_β are the spin-up and spin-down densities, respectively. The parameters a and b are those of Becke's exchange density functional [12], and were fitted to the Hartree–Fock energies of the rare gas atoms; the parameters c were obtained by adjustment to the "experimental" correlation energies of He and Ne. Note that B does not depend on the density and its derivative alone, but on the Kohn–Sham orbitals ψ_i as well. Our results are obtained with Hartree–Fock orbitals instead.

(b) The functional LYP is termed a "second-order gradient expansion" in ref. [2]. It is given by

$$\begin{aligned}E_{\mathrm{c}}={}&-a\int\frac{4}{1+d\rho^{-1/3}}\frac{\rho_{\alpha}\rho_{\beta}}{\rho}\\&-ab\int\omega\Bigg\{\rho_{\alpha}\rho_{\beta}\Bigg[2^{11/3}C_{\mathrm{F}}(\rho_{\alpha}^{8/3}+\rho_{\beta}^{8/3})+(\tfrac{47}{18}-\tfrac{7}{18}\delta)|\nabla\rho|^{2}-(\tfrac{5}{2}-\tfrac{1}{18}\delta)(|\nabla\rho_{\alpha}|^{2}+|\nabla\rho_{\beta}|^{2})\\&-\frac{\delta-11}{9}\left(\frac{\rho_{\alpha}}{\rho}|\nabla\rho_{\alpha}|^{2}+\frac{\rho_{\beta}}{\rho}|\nabla\rho_{\beta}|^{2}\right)\Bigg]-\tfrac{2}{3}\rho^{2}|\nabla\rho|^{2}+(\tfrac{2}{3}\rho^{2}-\rho_{\alpha}^{2})|\nabla\rho_{\beta}|^{2}+(\tfrac{2}{3}\rho^{2}-\rho_{\beta}^{2})|\nabla\rho_{\alpha}|^{2}\Bigg\}\,,\end{aligned}\qquad(2)$$

where

$$\omega=\frac{\exp(-c\rho^{-1/3})}{1+d\rho^{-1/3}}\rho^{-11/3}\,,\quad \delta=c\rho^{-1/3}+\frac{d\rho^{-1/3}}{1+d\rho^{-1/3}}\,,\quad C_{\mathrm{F}}=\tfrac{3}{10}(3\pi^{2})^{2/3}\,,$$

$$a=0.04918\,,\quad b=0.132\,,\quad c=0.2533\,,\quad d=0.349\,.$$

The parameters a, b, c and d in (2) were obtained by Colle and Salvetti from a fit to the He atom. Note that we have eliminated $\nabla^2\rho$ from formulae (21) and (22) of ref. [2] by partial integration, in order to save computing time.

The Gaussian basis sets used in the Hartree–Fock calculations are the same as in ref. [11] (those of ref. [13], extended with diffuse functions for the anions). The interatomic distances are the experimental ones [18].

The numerical integration scheme is related to that of Boys and Rajagopal [14] and to that of Becke [15]. The integrand is first partitioned into atomic contributions. The integrals obtained in this way are then integrated using the Patterson scheme [16,17]. With respect to Gaussian quadrature this has the advantage of allowing one to increase systematically the number of integration points. More details about the integration scheme will be published separately.

On the CRAY2 our program needs ≈ 15 μs per Gaussian-type function and grid point for the calculation of the density. The computation of the density gradient requires the same amount of time. The CPU time required to obtain the density functionals at each grid point is 40 μs for VWN, 60 μs for P, 50 μs for B and 40 μs for LYP.

Before showing the results, we discuss the effect of replacing the Kohn–Sham orbitals [19] by the Hartree–Fock ones. We will supplement the arguments given previously ([11], and references therein) with a calculation for Li^- with B and LYP. We have chosen this ion because it is known that correlation influences the density in this case relatively strongly [20,21]. This is due to:

(i) the diffuse character of the valence orbital;

(ii) the near-degeneracy, i.e. the important contribution of the p^2 configuration;

(iii) the fact that Li^- has a lower energy than Li only after correlation is included.

In order to study the role of density changes on the DF we improved the density with a multi-configuration self-consistent field calculation in the space of three s and one set of p orbitals. First, the two strongly occupied natural orbitals were used to construct the density. The correlation energy of Li^- was lowered by 1.7 mhartree both in B and LYP (2.6 mhartree in the local density approximation [4], 1.4 mhartree with self-interaction correction [5] and 1.6 mhartree with a gradient-corrected DF [9]). In another calculation, all the natural orbitals were used. The lowering was slightly more pronounced, but of the same order of magnitude: 3.3 mhartree with B, 1.9 with LYP (2.8, 1.5 and 1.7 mhartree with the other DFs mentioned above). It will be seen later that these effects are smaller by an order of magnitude than errors in the DF.

Note that in a variational Kohn–Sham calculation the lowering of the correlation energy would be partly compensated by an increase of the "Hartree–Fock" part.

3. Results

The correlation energies obtained with the two new DFs are shown in table 1. Differences between our values and those tabulated in refs. [1,2] arise for atomic densities: in the early work spherically averaged densities are used, whereas we construct ours from single-determinantal wavefunctions built with real spherical harmonics. (The maximum difference is for the O atom: 9 mhartree.) Lagovski and Vosko [22] argued that one should construct determinants which are eigenfunctions of the L_z operator with maximum M_L, i.e. use complex orbitals. In this case different ρ_α and ρ_β are obtained and, correspondingly, a correlation energy which is between our values and those of Becke. The criterion given by Lagovski and Vosko loses its applicability when

Table 1
Correlation energies obtained with the density functionals of Becke (B) and of Lee, Yang and Parr (LYP); values for spherically averaged atomic densities in parentheses

	B	LYP		B	LYP
H	0 a)	0 b)	N^-	236	235
He	42 a)	44 b)	O^-	299	299
Li	55 a)	53 b)	F^-	364	361
Be	92 a)	95 b)	LiH	85 a)	89 b)
B	125 (129 a))	126 (128 b))	BeH	105	107
C	163 (166 a))	160 (161 b))	BH	155	158
N	202 a)	193 b)	CH	197	197
O	262 (271 a))	258	NH	242	238
F	326 (333 a))	322	OH	304	301
Ne	391 a)	383 b)	FH	369	363
He^+	0	0	H_2	36	38
Li^+	50	48 b)	Li_2	131	133
Be^+	63	61	Be_2	195	195
B^+	107	107 b)	B_2	276	270
C^+	141	140	C_2	389	381
N^+	179	175	N_2	493	483
O^+	219	208	O_2	586	572
F^+	281	274	F_2	689	675
Ne^+	345	338	CH_4	297	294 b)
H^-	25	31	NH_3	323	318
Li^-	70	73	H_2O	347	341 (338 b))
B^-	138	136	C_2H_2	451	444
C^-	179	171	C_2H_6	562	549

a) Ref. [1]. b) Ref. [2].

spherical symmetry is absent (e.g. already for separated atoms on the hypersurface of a molecule). The dependence on the choice of the density is inherent to the existing density functionals, as it is for Hartree–Fock.

How do the DFs behave in the limiting cases of one-electron systems and of the homogeneous electron gas? In the first case, both B and LYP correctly reproduce zero correlation energy [1,2]. They both yield absolute values for the correlation energies of the homogeneous electron gas which are too small. For $r_s=(3/4\pi\rho)^{1/3}=2$ au we get 35 mhartree (27 mhartree) for B (LYP) instead of 45 mhartree in the paramagnetic case, and 13 mhartree (0 mhartree) instead of 24 mhartree in the ferromagnetic case. This is not critical, however, for small systems as experience has shown with another DF which behaves similarily [5]. In fact, the agreement for atoms is very good with LYP (largest error for Li is 8 mhartree [2]) and the results with B are only slightly worse (largest error is 13 mhartree, for N [1]). Unfortunately, the results are worse for many ions and molecules. As a result, correlation contributions to energy differences (ΔIE, ΔEA or ΔD_e) show larger errors. The same problem appeared also with other DFs (see, e.g. ref. [11]).

In figs. 1–5 we show the errors in ΔIE, ΔEA of the first-row atoms, ΔD_e of the first-row hydrides, ΔD_e of the first-row homonuclear dimers and the correlation contribution to the atomization energy of some polyatomic molecules (ΔE_a), respectively. They are defined as the difference between the calculated and the "experimental" [11] values. These values were calculated for different DF: (i) in the local density approximation (DF of ref. [4], values from ref. [11]), VWN; (ii) with gradient correction (DF of ref. [9], values from ref. [11]) P; (iii) B and (iv) LYP. In spite of the different nature of the DFs, the similarities in the trends shown in the figures are striking. We will thus refrain from discussing the figures in detail, as this can be found in ref. [11]. However, we would like to point out again that:

(a) the use of DFs generally improves the values of the ionization potentials, electron affinities and dissociation energies, as neither the over-, nor the under-estimation exceeds 100%; exceptions are ΔIE of Li and ΔD_e of BeH, but in these cases the absolute values are small, anyway;

(b) no DF reproduces well the changes in the correlation energy for every change in the occupation of a p orbital;

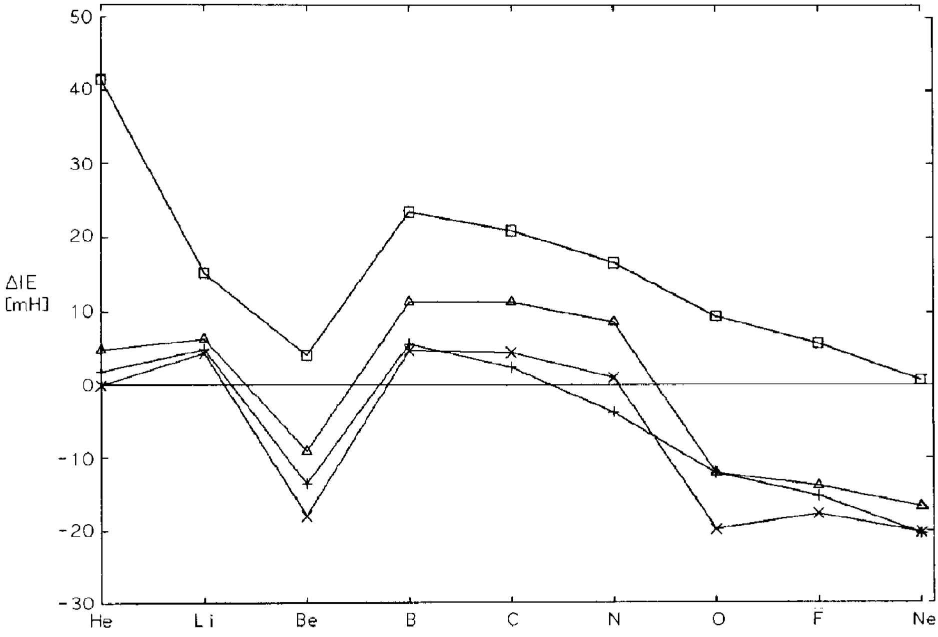

Fig. 1. Errors in correlation contributions to atomic ionization energies, ΔIE, in atomic units. (□) VWN; (△) P; (×) B; (+) LYP; the lines are used only to guide the eye.

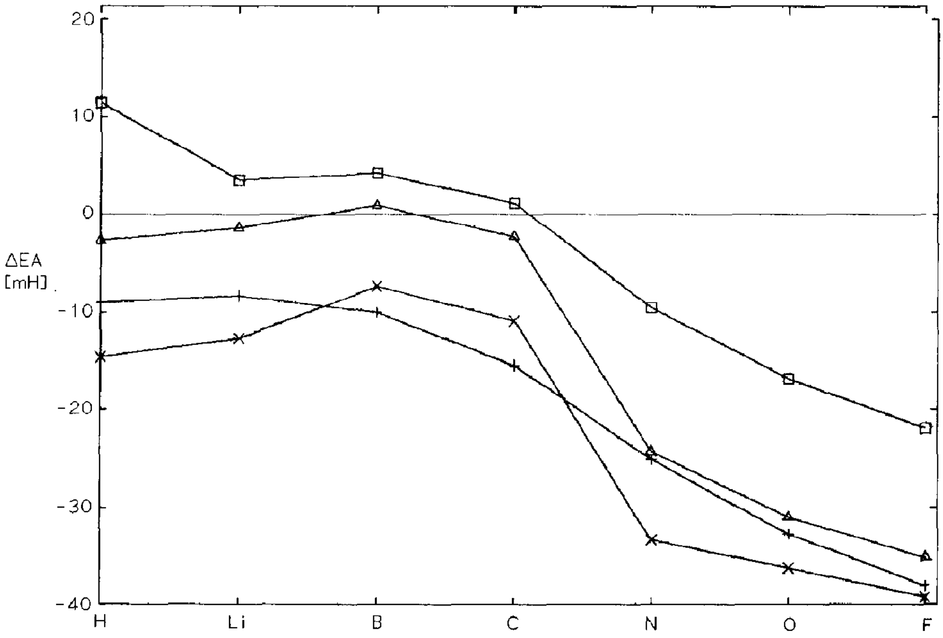

Fig. 2. Errors in correlation contributions to atomic electron affinities, ΔEA, in atomic units. (□) VWN; (△) P; (×) B; (+) LYP; the lines are used only to guide the eye.

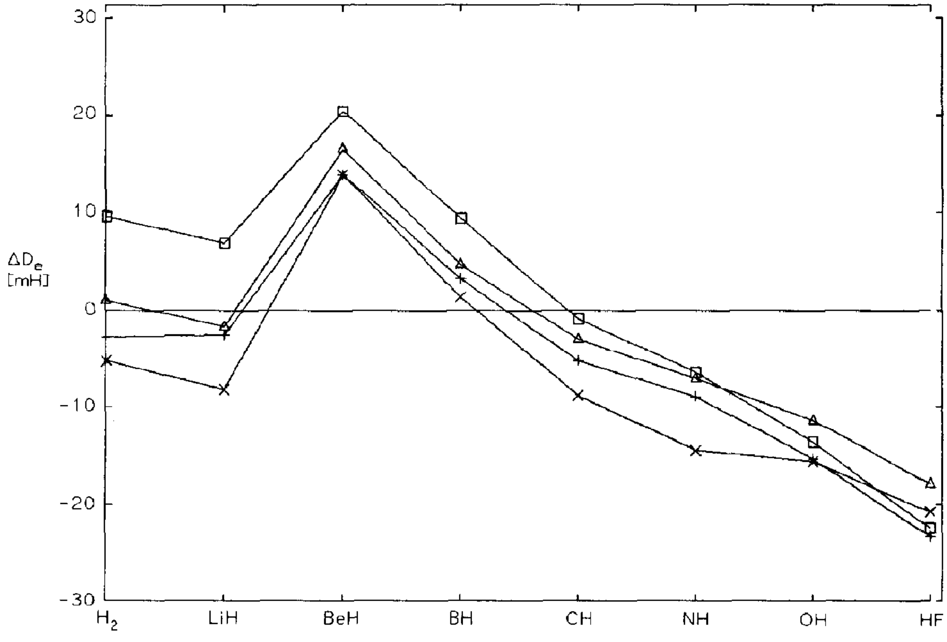

Fig. 3. Errors in correlation contributions to the dissociation energies of hydrides, ΔD_e, in atomic units. (□) VWN; (△) P; (×) B; (+) LYP; the lines are used only to guide the eye.

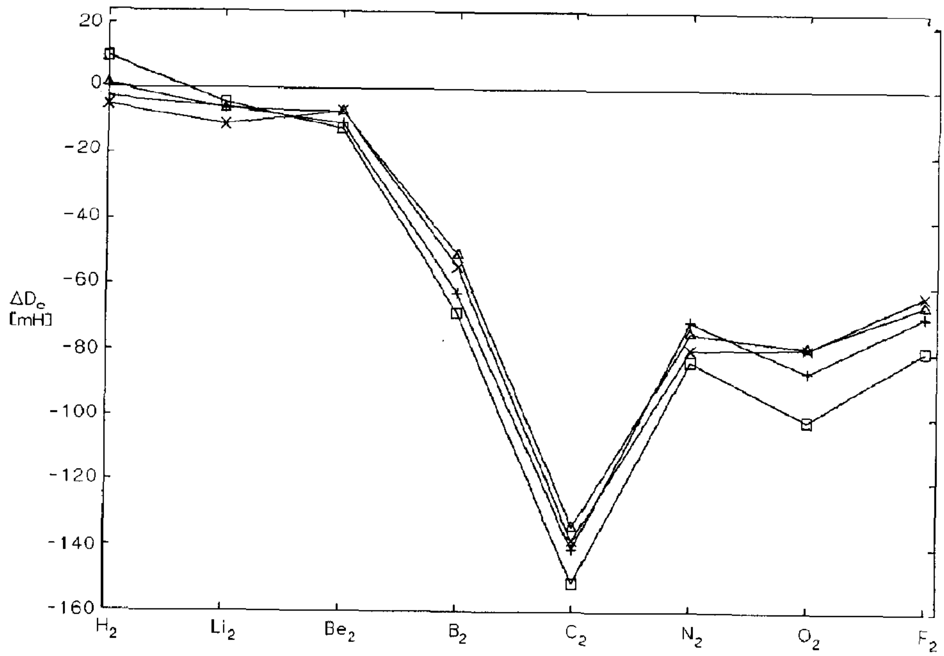

Fig. 4. Errors in correlation contributions to the dissociation energies of homonuclear dimers, ΔD_e, in atomic units. (□) VWN; (△) P; (×) B; (+) LYP; the lines are used only to guide the eye.

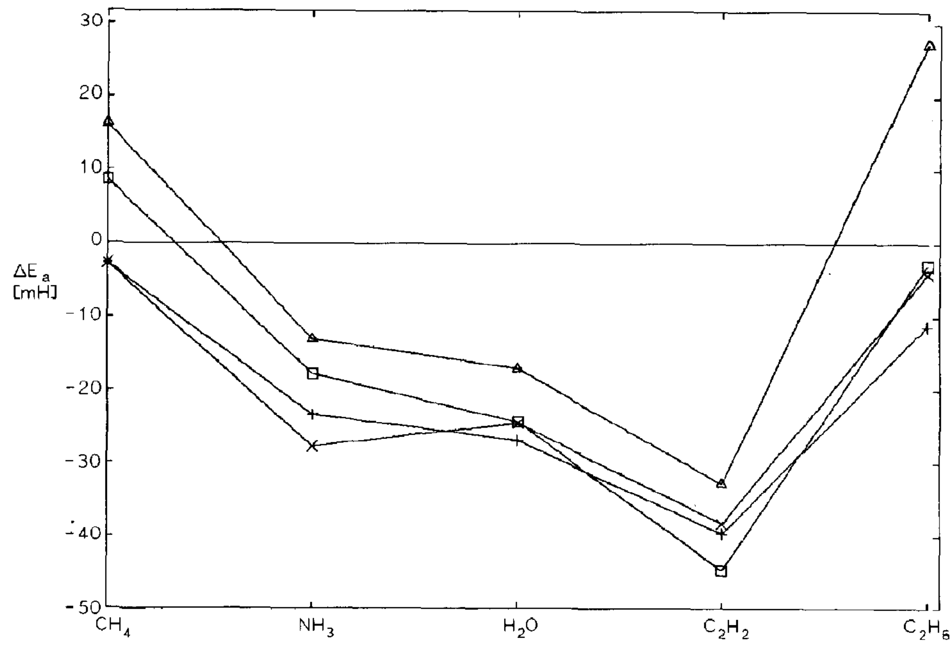

Fig. 5. Errors in correlation contributions to the atomization energies of some polyatomic molecules, ΔE_a, in atomic units. (□) VWN; (△) P; (×) B; (+) LYP; the lines are used only to guide the eye.

(c) in the case of hydrides, the absolute ΔD_e errors increase from the middle to the end of the first row, in accordance with (b);

(d) the most important errors occur for the ΔD_e of the homonuclear dimers (for C_2 the discrepancy between the DF and the exact value is greater than 100 mhartree);

(e) the errors change significantly in an isoelectronic series (e.g. for the ΔE_a of CH_4, NH_3 and H_2O or of C_2H_6 and F_2).

Due to the magnitude of effect (d), we believe that the elimination of this source of error is essential for improving correlation energy DFs. It is surprising that the results are better when using DFs for both exchange and correlation [23]. Thus, we feel that it might also be possible to find improved approximations for correlation energy DFs, along the lines followed in refs. [1,2]. Another way of reducing this error is to include near-degeneracy effects explicitly in wavefunction calculations, while the rest of the correlation energy is covered by a DF. A double-counting of the correlation energy can be avoided, as shown in ref. [24]. In this way, improved values for ΔD_e, ΔIE and ΔEA are obtained (errors about 10 mhartree [24,25]).

4. Conclusion

The new density functionals of Becke and of Lee, Yang and Parr have been tested for systems containing first-row atoms. Despite good atomic total correlation energies, the correlation contributions to ionization energies, electron affinities and dissociation energies still show errors of several tens of mhartree. In contrast to wavefunction methods this error cannot be reduced systematically. As an improvement over Hartree–Fock is achieved, however, in nearly all cases, we believe that density functionals are a useful tool for obtaining estimates of correlation energies.

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